

Robust On-Line Measurement of Conversion and Molecular Weight Using NIR Spectroscopy During Solution Polymerization

A. CHERFI,¹ G. FEVOTTE,¹ C. NOVAT²

¹ LAGEP UMR CNRS 5007, Université Claude Bernard Lyon 1, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne CEDEX, France

² CNRS-LCPP/ESCPE, Université Claude Bernard Lyon 1, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne CEDEX, France

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ABSTRACT: Fiber-optic near-infrared (NIR) spectroscopy was used to monitor the monomer conversion and the weight-average molecular weight of the polymer produced during solution polymerization of methyl methacrylate (MMA) carried out in a lab-scale reactor. NIR spectra were recorded during batch and semi-continuous reactions using an *in situ* transmission probe. Off-line gravimetry and GPC were used as reference methods to provide the conversion and the average molecular weight data set required for the calibration procedure. A statistical model was generated using partial least-squares regression (PLS) to relate the NIR spectral data to the two polymerization variables of interest. The measurements were then validated for various operating conditions (i.e., different solvent, initiator, MMA, and chain-transfer agent concentrations) and for both batch and semi-continuous modes. The conversion was predicted during three validation experiments with an average standard error of prediction (SEP) of 2.1%. The on-line evaluation of \bar{M}_w was obtained with an average relative SEP of 5.7%; such on-line NIR measurement was thus demonstrated to be robust and accurate, even in the case of versatile use of the polymerization plant. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2510–2520, 2002

Key words: infrared spectroscopy; sensors; molar mass distribution

INTRODUCTION

To improve the safety, the productivity, and the reproducibility of polymerization processes, the development of robust and accurate on-line sensors still remains a key issue. Obviously, the availability of new real-time information about a polymerization process allows one to monitor more pertinently the progress of the reaction, to analyze the effects and the causes of potential

disturbances, and, consequently, to develop more advanced control policies. Due to the increasing demand for the production of polymers with pre-specified properties, great attention is now being given to finding rapid, reliable, and relevant methods by which the mastery over industrial production can be improved. Actually, even though this remains difficult, it is clear that an “ideal” control situation is ensured when one is in a position to monitor both the reaction rate(s) [i.e., the overall or individual monomer conversion(s)] and any variable related to the quality of the polymeric product. From this point of view, the molecular weight (MW) of the polymer is of

Correspondence to: G. Fevotte (fevotte@lagep.cpe.fr).

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capital importance during its synthesis and when considering its applications, as most properties which are specific to polymeric materials come from their high molecular masses.¹

Among the sensing technologies, near-infrared spectroscopic (NIRS) techniques are really promising and significant efforts are now being devoted to the development of on-line equipment where the spectrophotometers traditionally used in the laboratory may be displaced to the industrial environment in a remote manner through the use of fiber-optic waveguides. *In situ* measurements were thus demonstrated to be possible for a number of applications. NIR spectroscopy is well suited to provide real-time structural and kinetic data without complicated hardware developments. The NIR spectral region, which covers the range from 700 to 2500 nm, expresses much of the chemical and structural information on the reaction medium, but the information tends to be in broad and overlapped bands. The processing of NIR spectral data has been shown to allow real-time evaluation of key parameters such as monomer concentration(s) or potential fluctuations of the quality of raw materials² or to evaluate more specific variables such as the acid value during polyester production,³ density and melt index of polyethylene,⁴ the average particle diameter during emulsion⁵ or suspension^{6,7} polymerization processes, or the polymer composition during extrusion processes.⁸ Due to the variety and the complexity of the NIR spectral data, it is necessary to use "black-box" and multivariate data-processing models to extract the criterion of interest among all information contained in the recorded spectra. The "parameters" of such models are computed from a calibration data set and should be validated thereafter. The success of further on-line predictions depends on various criteria: the sampling technique, the off-line measurement method which was used, and, finally, the processing algorithm applied to the spectrum to draw the appropriate criterion.

Several sensors for measuring on-line the monomer conversion were described in the literature, such as refractometry,^{9,10} densimetry,^{11,12} calorimetry,¹³⁻¹⁹ and ultrasound measurements.^{20,21} *In situ* probes are available for these techniques, which solve many difficulties arising from the use of complex sampling devices. However, some of these techniques, such as chromatography,^{9,22} deal with diluted systems and can require sampling devices leading to undesirable measurement delays. Moreover, some *in situ*

techniques, such as densimetry or ultrasound spectroscopy, do not seem to be robust enough, essentially because they require complex modeling involving numerous and poorly known physical and physicochemical parameters. This explains why on-line spectrometry is promising for the measurement of conversion, even though it requires extensive, cautious, and time-consuming calibration. As outlined by Gossen et al.,⁵ early papers relating the use of NIR spectroscopy for the measurement of monomer conversion or copolymer composition have almost been ignored by the polymer industry, while numerous papers were devoted to various applications in the field of agriculture and in the food industry. Even though the potential of in-line NIR techniques is now well established, it appears that most articles are focused on the monitoring of extrusion processes^{8,23} or cure reactions,^{9,24} rather than on the control of bulk, suspension, or emulsion polymerization reactions. Long et al.² used NIR spectroscopy to monitor monomer conversion during anionic solution polymerization; the conversion of the vinyl protons in the monomer to methylene protons in the polymer was measured under conventional (10–20% solids) solution polymerization conditions. Gossen et al.⁵ showed that advanced calibration techniques applied to both UV and NIR spectra allowed one to predict the concentration of all the major components involved during the semibatch emulsion copolymerization of styrene and methyl methacrylate (MMA). The mean particle size was also predicted for some of the calibration sets. Dallin³ also discussed some of the issues and solutions raised by process NIR analysis. As an example, the monitoring of a polyester reaction was briefly reported. A recent article²⁵ reported the use of both attenuated total reflectance mid-infrared (ATR FTIR) and NIR spectroscopy to the on-line monitoring of the solution polymerization of MMA in toluene. The authors found NIR spectroscopy to be more practical than ATR FTIR spectroscopy for implementation as an industrial routine tool.

The determination of the molecular weight distribution (MWD) of a polymer can be carried out by various methods based upon the properties of solutions. The techniques which are reported in the literature⁹ for the on-line measurement of molecular weight are essentially based on viscosimetry and gel permeation chromatography (GPC), but most of the available technologies are difficult to implement and only provide indirect information on the MWD of the polymer. More-

over, in the case of on-line GPC, complex sampling devices are required,^{26–28} measurements may be corrupted by noise,⁹ and the duration of the analysis of a given sample leads to excessive time delays.²⁷ For example, Jo and Bankoff²⁹ used on-line measurements of conversion and viscosity to estimate \bar{M}_w during the solution polymerization of vinyl acetate, carried out in a continuous stirred tank reactor. The authors developed a model relating the molecular weight to the viscosity and the monomer conversion; it was, however, difficult to separate the effect of the two parameters in question. In the same vein, several works were published about the use of falling-piston or vibrating on-line viscosimeters to monitor variables which can be related to the MWD of the polymer produced using various polymerization technologies.^{26–30} Useful but indirect information was thus obtained.

As for the measurement of conversion, NIRS can certainly be applied to the monitoring of molecular weight during polymerization processes, but to the best of our knowledge, no such application has been reported. Our purpose was to assess the feasibility of monitoring both the monomer conversion and the weight-average molecular weight during typical solution polymerization reactions, using on-line NIRS. Particular attention was focused on the robustness of the calibration when various operating strategies were applied. Indeed, unless cautious and systematic experimental work is performed, it is our experience that the calibration models are very sensitive to operating situations or disturbances which were not taken into account during the collection of the calibration data set. It is therefore an important issue to demonstrate the flexibility of NIR monitoring when significant variations of the composition of the reaction mixture are encountered and in the case of various manipulations of the inlet streams [i.e., batch or semi-continuous processes, semicontinuous feeding with monomer and/or with solvent, use of chain-transfer agents (CTA)].

In the following, it is shown that solution batch and semi-continuous homopolymerization of MMA in toluene can be monitored using an *in situ* NIR probe. Standard software calibration tools were applied to experimental data sets obtained from off-line gravimetric measurements of conversion and GPC measurements of \bar{M}_w . The performances of NIRS to predict the conversion and \bar{M}_w profiles were then assessed for various typical operating situations.

EXPERIMENTAL

Figure 1 represents a schematic of the experimental device used. The solution polymerization of MMA in toluene was carried out in a semi-continuous well-mixed 1-L reactor. The stirring rate was kept constant at 240 rpm. The reactor was equipped with a glass jacket and a condenser. Water was circulated through the jacket to maintain the reaction medium at 70°C. The supervision of the process was ensured using a microcomputer connected to an HP 34970A data acquisition and control system. The reactor and jacket temperatures were recorded on-line. Real-time manipulations of the inlet flow rates were eventually controlled using outputs of the HP control system which was connected to the analog input of two Prominent® dosing pumps.

The initial heel of the reactor was composed of a solvent (toluene, P.A.), monomer (MMA, 99% purity), and initiator (AIBN, 98% purity), all provided by Acros Organics (Noisy-le-Grand, France), and distilled under reduced pressure. For some experiments, a CTA was used, dodecyl mercaptan (98%), which was provided by Aldrich (L'Isle d'Abeau, France). The reactants were degassed for approximately 0.5 h before beginning the reaction. During the reaction, the reactor was fed with nitrogen. The reaction conditions and flow rates are given in Table I. The initial charge was fed to the reactor and the temperature was increased to its setpoint value. Once the steady-state temperature was obtained, solubilized AIBN was introduced. When semicontinuous operations were performed (see Table I), monomer or solvent was injected at the appropriate rate and time. As Table I shows for runs 5, 9, 10, and 14, CTA injections were added to the reactor to assess the insensitivity of the NIR measurements of conversion when such reactants were used during the reaction to control the MWD. This point had to be checked as we aimed at dealing, during further work, with on-line control policies of MWD.

During every reaction, about 20 samples were withdrawn using the bottom jacketed valve of the reactor for gravimetric measurements of conversion. About eight samples per reaction were also analyzed using GPC. The mass of the samples was measured for further computations of the composition of the reacting medium, in the case of a semicontinuous operation. The polymerization of the gravimetric samples was stopped using both hydroquinone as an inhibitor and dilution in

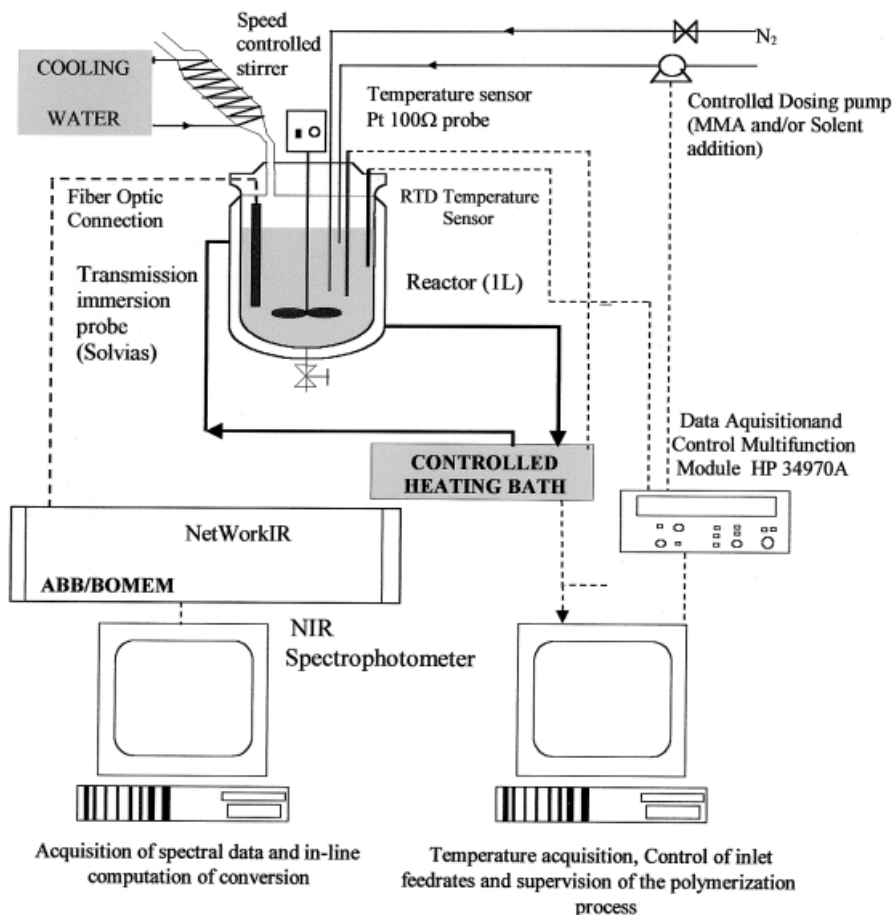


Figure 1 Experimental setup: lab-scale semi-continuous polymerization reactor equipped with an *in situ* NIR transmission probe.

a cold solvent with an approximate mass ratio of 1/3. The off-line measurements of conversion were performed to obtain a set of calibration data using an infrared thermobalance LJ16, marketed by Mettler. The off-line measurements of \bar{M}_w were performed to obtain a set of calibration data using a GPC unit equipped with a Waters 410 differential refractometric detector, a Waters 717 plus autosampler, and a Waters 515 HPLC pump and furnace. Two columns with a porosity of 10^5 \AA (Waters Styragel HR5E) and a column with a porosity of 10^4 \AA (Waters Styragel HR4E) were used. The samples were first dissolved in tetrahydrofuran with an approximate mass ratio of 1%; the eluent was then circulated in the columns with a constant flow rate (1 mL/min).

The spectral analysis in the NIR region was carried out by an industrial NetWorkIR spectrophotometer marketed by ABB/Bomem, which is a dispersive NIR device, sweeping the spectral area extending from 700 to 2500 nm. An immersed

transmission probe, provided by Solvias, was connected to the spectrophotometer using fiber optics. The probe, which allows one to adjust the double-path transmission, was tuned with an effective optical way of 6 mm. The analysis of the NIR data was carried out by using Grams 32 (version 5.0), a spectral analysis software provided with the NIR instrument.

First, a calibration model was established for similar MMA batch polymerization operations in toluene, based on the same operating conditions (i.e., temperature and initial MMA and AIBN fractions were kept constant). The results obtained after such calibration were very accurate. A reliable calibration model for conversion measurements was obtained from a reduced set made up of only 20 data points. However, such calibration turned out to be irrelevant for the monitoring of batch processes where variations of the operating parameters were deliberately introduced. As displayed in Table I, three series of semicontinu-

Table I Experimental Conditions of the Batch and Semi-Continuous Polymerization Runs Used for the Set of Calibration Data

Run (Ref.)	MMA ^a (g)	Toluene ^a (g)	AIBN ^a (g)	Feeding Policy: Total Mass (g) and Injection Time (min)	Corresponding Inlet Flow Rates (g/s) and Duration of Feeding (min)
Run 1	240	560	1.818	—	—
Run 2	240	560	2.728	—	—
Run 3	320	480	1.5	—	—
Run 4	200	600	3.194	—	—
Run 5	240	560	2.780	CTA: 4.47–0	0.894–0.083
Run 6	320	480	2.707	—	—
Run 7	240	560	3.637	—	—
Run 8	340	360	1.5	—	—
Run 9	340	360	1.5	CTA: 2.910–30	0.582–0.083
Run 10	320	483	1.819	CTA: 2.068–120 } Toluene: 84.1 } CTA: 4.3 } ^b	0.414–0.083 ^b
Run 11	320	180	1.107	Toluene: 300–2	0.032–156
Run 12	321	282	2.019	Toluene: 200–0	0.014–238
Run 13	208	251	1.546	Toluene: 196–0	0.014–233
Run 14 ^c	340	100	1.5	Toluene: 257–10	0.038–113
Run 15	200	323	1.45	MMA: 272.9–0	0.018–253
Run 16	170	480	1.81	MMA: 169.2–0	0.012–235
Run 17	140	560.2	1.82	MMA: 95.6–0	0.0044–362
Run 18	200	300	2	MMA: 199.5–0	0.018–185

^a Mass in the initial charge.

^b Both toluene and CTA were introduced after 61 min. The duration of the injection was about 5 s.

^c CTA initial mass = 3 g; $T = 70^{\circ}\text{C}$; CTA: dodecyl mercaptan (DDM).

ous operations were then performed, with various MMA, CTA, and toluene feeding policies. During these experiments, the total amount and the time and duration of the reactant injection were changed.

NIR MONITORING OF CONVERSION

Calibration of the Measurement of Monomer Conversion

To establish the calibration of the NIR measurements, batch MMA solution polymerization operations with different MMA, CTA, and AIBN contents and semicontinuous MMA solution polymerization with operations solvent, MMA, and CTA addition at different flow rates were carried out, according to the procedure presented previously.

Figure 2 represents the time variations of the NIR spectra during run 14. The absorbencies

were computed as the average of 113 scans per measurement; the resolution was set to 16 cm^{-1} . The spectra clearly outline the decrease of two peaks located at 6167 and 4744 cm^{-1} , respectively, which are associated to decrease in the MMA concentration. The two bands are assigned to the first overtone of the $2\nu(\text{CH}_2=)$ absorption and to a combination of the $\nu(\text{CH}_2=)$ and $\delta(\text{CH}_2=)$ modes, respectively.²⁵

The spectral data recorded during the different polymerization calibration operations were entered into the “Grams 32” chemometrics software. The measured spectral variations were related to the gravimetric values of the conversion which were measured off-line. A calibration model correlating absorbance to conversion was then computed, using the two “interesting” spectral regions, with an automatic baseline correction. A standard available partial least-squares regression (PLS) software was applied to the data processing.

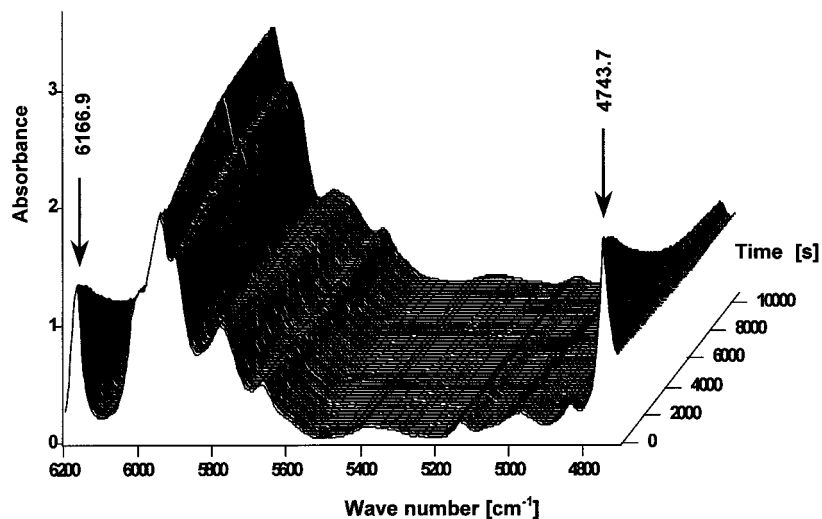


Figure 2 Time variations of the NIR spectra during the reaction run 14.

Figure 3 represents the conversion profiles $x(t)$ obtained from the gravimetric data during the different runs described in Table I. The data points outline the variability of operating conditions in

terms of the overall reaction rate: The conversion after 6 h evolves between 69 and 99% (i.e., between runs 17 and 7). For example, run 15 takes more time and exhibits a specific conversion profile, due

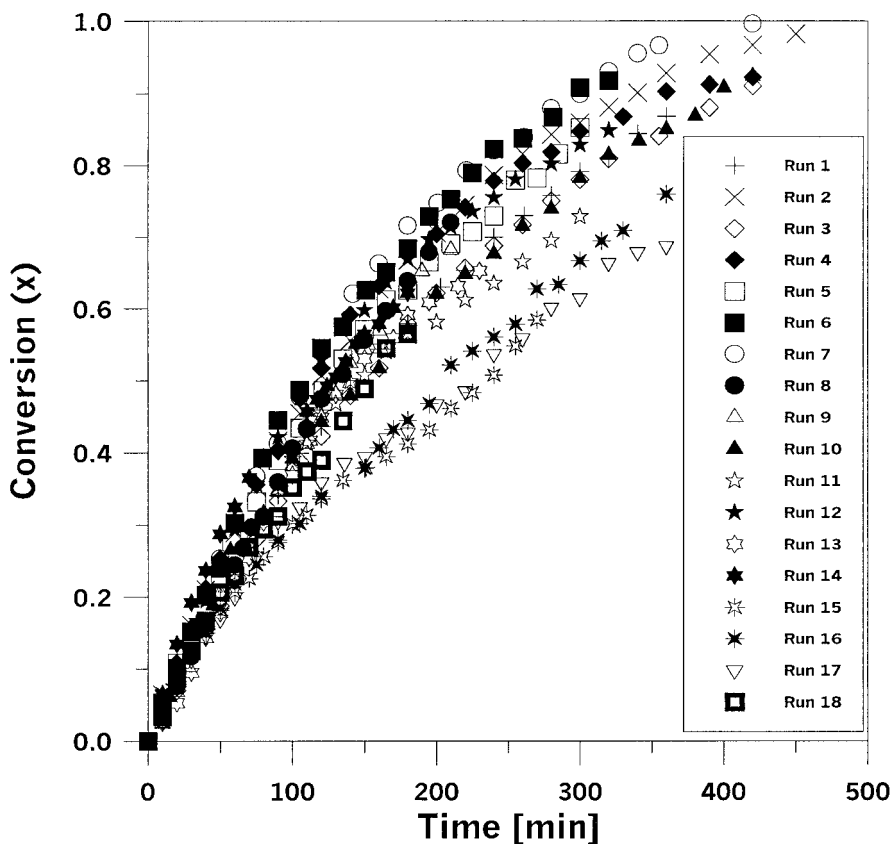


Figure 3 Calibration data set: gravimetric conversions against time.

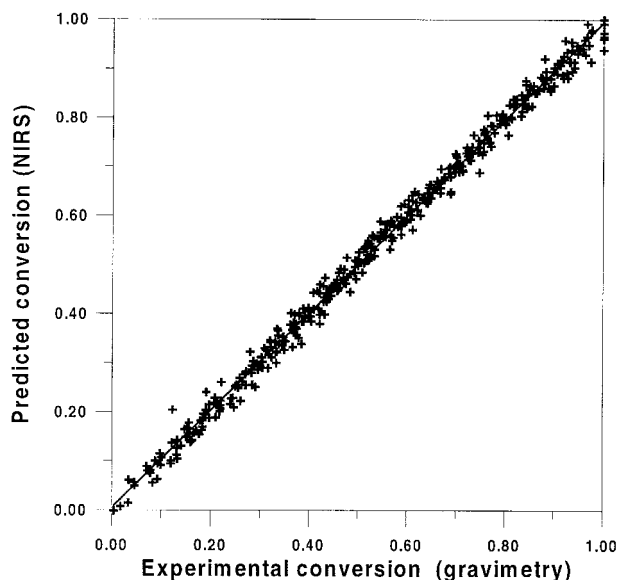


Figure 4 Calibration data set: predicted against measured conversion.

to the semicontinuous feeding program which was applied. The PLS procedure finally resulted in a nine-factor model, and the corresponding correlation coefficient was found to be 99.45%. The standard error of calibration (SEC) was equal to 1.95%.

Figure 4 represents the conversions computed from the recorded NIR spectra against the gravimetric conversions introduced in the calibration data set. If one considers the large variety of operating situations leading to a wide range of conversion profiles, the results are very satisfactory.

Validation of the On-line Measurement of Conversion Using NIR Spectroscopy

It is essential to assess the predictive capabilities of the PLS model through the on-line application

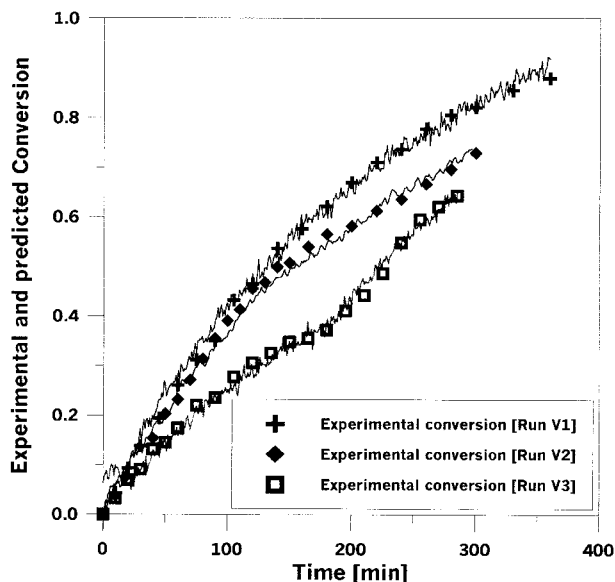


Figure 5 Validation of the NIR measurement of conversion: measured and predicted conversion against time for runs V1, V2, and V3. The lines represent the NIR predictions.

of the calibration to the monitoring of polymerization operations which were not taken into account during the calibration procedure. With this aim in view, three extra runs were performed for validation purposes. The experimental conditions were deliberately chosen with significantly different parameters. As one can see in Table II, run V1 is a simple batch operation, run V2 is a semicontinuous reaction which was fed with the solvent at a constant flow rate, and run V3 is a semicontinuous reaction fed with MMA.

Figure 5 represents the conversion trajectories “predicted” by the PLS model and the conversion measured using gravimetry. A perfect agreement between the measured and predicted values is

Table II Experimental Conditions of the Batch and Semi-Continuous Polymerization Runs Used for the Set of Validation Data

Run (Ref.)	MMA ^a (g)	Toluene ^a (g)	AIBN ^a (g)	Feeding Policy: Total mass (g) & Injection Time [min]	Corresponding Inlet Flow Rates (g/s) and Duration of Feeding [min]
Run V1	320	480	1.804	—	—
Run V2	320	160	1.107	Toluene: 160–0	0.053–50
Run V3	100	400	2.290	MMA: 316.2–0	0.043–60 0.029–182

^a Mass in the initial charge; $T = 70^{\circ}\text{C}$.

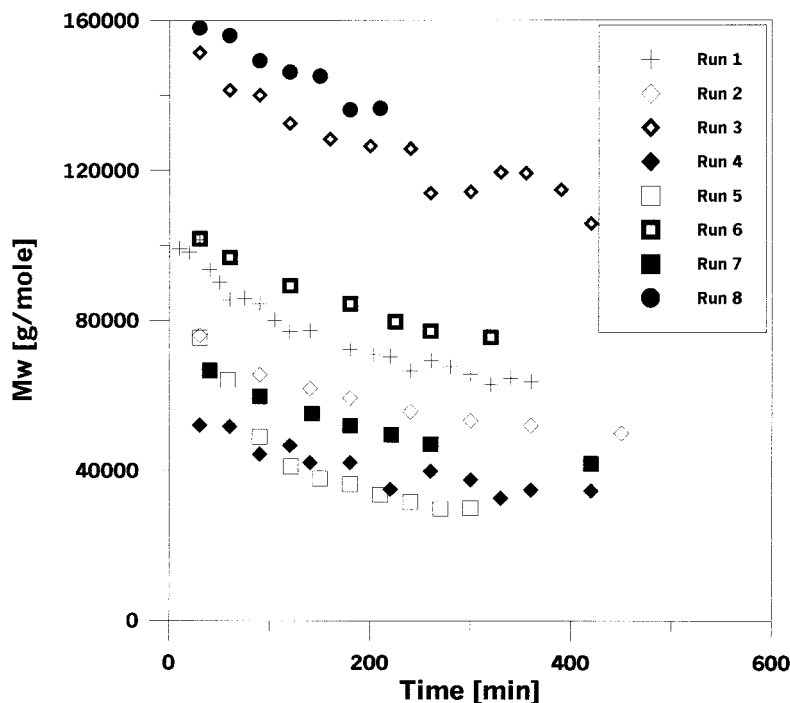


Figure 6 Calibration data: \bar{M}_w measured using GPC against time for batch processes, runs 1–8.

clearly demonstrated, whatever the operating strategy. The standard error of prediction (SEP) was computed to be equal to 1.89% for run V1, 1.87% for run V2, and 2.58% for run V3. The SEP was found to be larger after run V3, which is a consequence of the significant relative uncertainty observed at the beginning of the reaction (see Fig. 5). As the initial volume of the reaction medium was low in this case, such an initial loss of accuracy was attributed to the fact that the probe was insufficiently immersed in the solution. Given the accuracy which is usually expected from gravimetric measurements, the quality of the NIR measurements is undeniable.

NIR MONITORING OF THE WEIGHT-AVERAGE MOLECULAR WEIGHT

Calibration of the Measurement of \bar{M}_w

Figures 6 and 7 represent the large distribution of \bar{M}_w data obtained from samples withdrawn during the different runs described in Table I and analyzed using GPC. As expected, the average molecular weight decreases with time during the batch experiments, and the various molecular

weight profiles obtained are consistent with the initial monomer and initiator concentrations. The effect of CTA in the initial heel or after semi-batch addition is also clearly observed (see run 5). For semicontinuous operations fed with the monomer, \bar{M}_w can be stabilized if the feed flow rate remains moderate (see run 17) or if it increases with high monomer feed rates (runs 15 and 18). \bar{M}_w is maximized and reaches 194,100 g/mol after 270 min during run 15, which corresponds to the highest final MMA content. As expected, the smallest \bar{M}_w values were obtained during the semicontinuous reactions fed with the solvent and CTA (run 14).

The application of PLS regression in the spectral regions going from 1600 to 1640 nm and 2090 to 2130 nm results in a PLS model with seven factors. The correlation coefficient is 97.41% and the SEC is equal to 5972 g/mol, which corresponds to an average relative SEC equal to 5.14%. Figure 8 represents the plot of the NIR predicted \bar{M}_w values against the off-line GPC data for the whole calibration data set. Given the wide range of experimental data and the diversity of operating conditions involved during the calibration experiments, these results are very satisfactory.

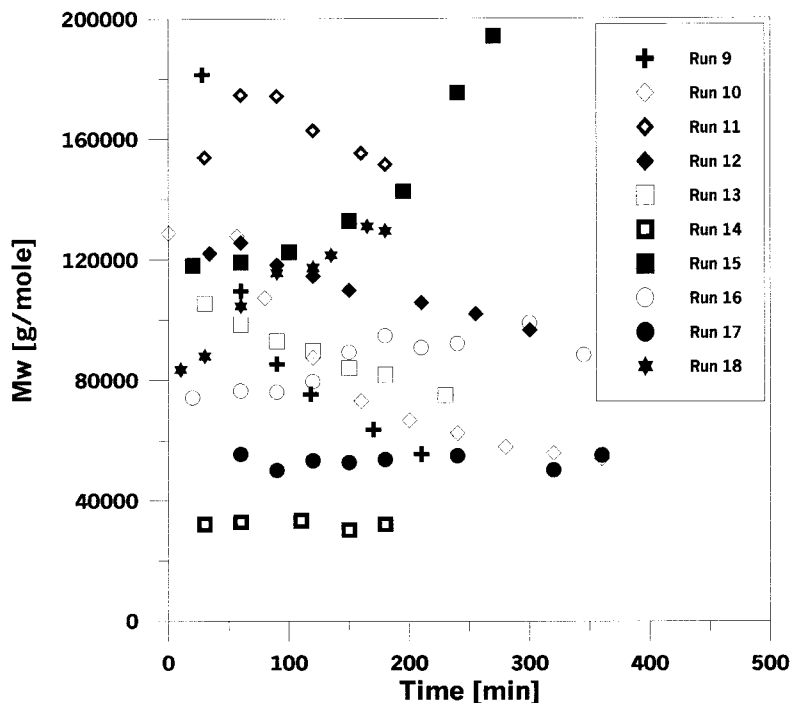


Figure 7 Calibration data: \bar{M}_w measured using GPC against time for semi-continuous processes, runs 9–18.

Validation of the On-line Measurement of \bar{M}_w Using NIR Spectroscopy

As for the conversion measurements, the capabilities of the PLS model to evaluate \bar{M}_w on-line

were tested during three extra runs performed for validation purposes (see Table II). Figure 9 represents the time variations of \bar{M}_w which were

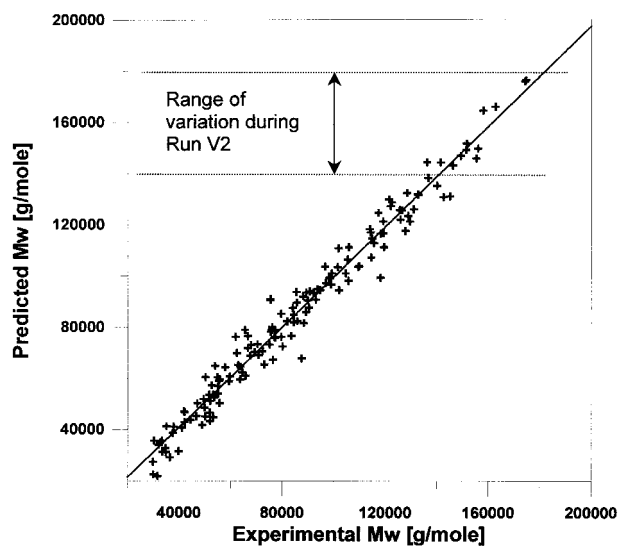


Figure 8 Calibration of the NIR measurement of the average molecular weight: predicted against measured \bar{M}_w (calibration data set).

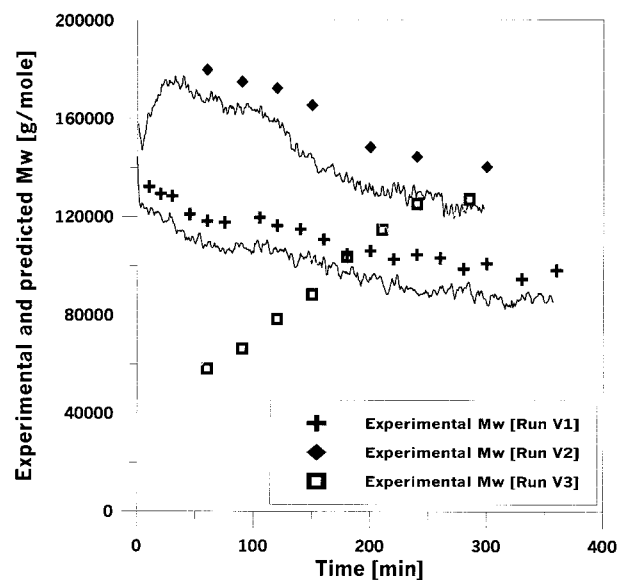


Figure 9 Validation of the NIR measurement of the average molecular weight: measured and predicted \bar{M}_w for runs V1, V2, and V3. The lines represent the NIR predictions.

predicted by the PLS model. The off-line experimental values of \bar{M}_w measured using GPC are also displayed in Figure 9. As one can see, the predicted values of \bar{M}_w fit rather satisfactorily the reference off-line GPC data, whatever the operating strategy. Based on these results, the SEP was computed after runs V1–V3 and found to be equal to 6036, 14,032, and 4683 g/mol, respectively. These absolute errors correspond to relative uncertainties of 4.8, 7.9, and 4.4%, respectively. The accuracy of the MWD measurements using GPC is generally expected to be of the order of 10%; it can be reduced if the standard polymer samples used for calibration are similar to the polymer under investigation. The quality of the NIR estimates is therefore very good, compared with the reference technique used. It turns out that the SEP is significantly higher for run V2, which is not a surprising result as the molecular weights produced during the fed-batch operation in question are located in the upper side of the calibration set. As one can see in Figure 8, only 11 reference data are available in the range of molecular weight produced during run V2. However, if one considers the accuracy which is generally expected from GPC measurements, the quality of the NIR predictions is rather good.

CONCLUSIONS AND PERSPECTIVES

Many difficulties encountered in the monitoring and control of polymerization reactors arise from the lack of efficient on-line sensors. Most variables related to the quality of the polymeric materials—in particular, the molecular weight distribution—are not available during the reaction process, and even the measurement of monomer conversion(s), which obviously appears as a prerequisite for any feedback control application, remains difficult to perform on-line. In such a context, infrared spectroscopic techniques and, more specifically, NIR technologies associated with fiber-optic probes, are very promising since they can provide structural and kinetic data in real time and without requiring any sampling system. However, even though the potential of on-line NIR techniques is now well established, published articles relating applications of NIR measurements to the monitoring of conversion during polymerization reactions are still rare.

The aim of the present article was to assess the performances of fiber-optic NIR spectroscopy for the monitoring of the solution homopolymeriza-

tion reaction of MMA in toluene. The NIR spectra were found to be sensitive to the polymerization advancement in the wavelength tapes (1600–1640 and 2090–2130 nm). A “standard” PLS regression was used for the calibration of the measurements of conversion, X , and weight-average molecular weight, \bar{M}_w . The calibration data set was obtained using off-line gravimetry and GPC to evaluate the conversion and \bar{M}_w of samples withdrawn during 18 polymerization batch and fed-batch experiments. The correlation coefficients of the calibration model for X and \bar{M}_w were found to be 99.5 and 97.4%, respectively, while the average SEC was equal to 2 and 5.1%, respectively.

The calibration was then validated through the monitoring of conversion during three different batch and semi-batch operations. The obtained NIR predictions of conversion were found to be accurate, with average SEPs equal to 2.1%, and the on-line evaluation of \bar{M}_w was obtained with an average relative SEP of 5.7%. To be more convincing for industrial applications, it was important to demonstrate the robustness of the technique in terms of the versatility and multipurpose use of the NIR equipment. To the best of our knowledge, successful NIR applications to the on-line monitoring of polymerization reactions were only reported in the case of well-defined processes. The present study shows that key variables of the polymerization system can be estimated on-line with no particular limitation concerning the operating conditions (i.e., pure batch or any kind of feeding strategy). While the obtained calibration model accounts for variable amounts of toluene in the reactor, it should be noted that new experimental data would have to be introduced in the calibration set if the use of other solvents was envisaged. The reported results therefore open up new perspectives for the on-line feedback control of the polymerization advancement. Such control should allow improvements in the safety, the productivity, and the reproducibility of the reaction. Using NIR measurements, variables characterizing the polymeric product could also be more efficiently mastered, which is a prerequisite for obtaining materials with prespecified properties.

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